A DIFFERENTIAL THERMAL

ANALYSIS OF CERTAIN CLAY MINERALS

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May 1953

THESIS
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A DIFFERENTIAL THERMAL ANALYSIS

OF

CERTAIN CLAY MINERALS

Submitted to the Faculty of

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In Partial Fulfillment of the Requirements
for the Degree of
Master of Civil Engineering

by

Milton J. Harcar, Jr.
and
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SYNOPSIS

This paper describes certain refinements of the apparatus and procedure used in differential thermal analysis of clay minerals. These refinements are aimed at standardizing the conditions within the sample holder cells so as to minimize experimental errors. More important, this paper offers evidence that, though the base line of the differential thermal curve is displaced from the zero millivolt line, it is not necessarily parallel to the zero millivolt line.

Differential thermal curves are given for stated weights of several of the standard clay minerals. The results of differential thermal analysis of four unknown clay soils are given.

This paper analyzes the data obtained from a number of tests and concludes that inaccuracies inherent in the differential thermal method of analysis preclude the use of this method for quantitative analysis of the clay mineral composition of soils.

SYNOPSIS

RECORD OF TESTS CONDUCTED

I- EFFECT OF ADMIXTURE OF INERT STANDARD

Clay Sample used-	Halloysite H-12 Bedford, Ind.
Grain Size	200-pan
Treatment	Oven dried for 24 hours at 50°C

Mixture	No. of Tests
0.6 grams H-12	7
0.6 gr. H-12 plus 0.1 gr. Alumina	3
0.6 gr. H-12 plus 0.2 gr. Alumina	3
0.6 gr. H-12 plus 0.3 gr. Alumina	5

II- [illegible]
(Grain size 200-pan --- Oven Dried 24 hours at 50°C)

Sample	Weights	No. of Tests
H-4	0.5 grams	3
	0.6 "	4
	0.7 "	5
	0.8 "	5
H-12	0.5 "	5
	0.6 "	7 (same as in I above)
	0.7 "	3
	0.8 "	3
H-24	0.5 "	5
	0.6 "	4
	0.7 "	4
	0.8 "	6
H-32	0.5 "	5
	0.6 "	3
	0.7 "	4
	0.8 "	4
H-36	0.5 "	3
	0.6 "	4
	0.7 "	3
	0.8 "	4

SYNOPSIS

RECORD OF TESTS CONDUCTED (Cont.)

III- THERMOGRAMS FOR UNKNOWN CLAYS

(Grain Size 200-pan --- Oven Dried for 24 hours at 50°C --- All weights 0.7 gram of sample)

Sample	No. of Tests
Unknown Clay (From site of New RPI Dorms)	3
Bleu Brick Yard Clay	4
Lake Albany Clay - 152' Depth	3
Lake Albany Clay - 83' Depth	3

Samples treated with H_2O_2, then oven dried for 24 hours at 50°C.

Lake Albany Clay - 152' Depth	1
Lake Albany Clay - 83' Depth	1

IV- DETERMINATION OF DISPLACED BASE LINE

Sample	Cooling Curves	Reheat Curves
H-4		2
H-12		2
H-24	1	3
H-32		2
H-36		3
Unknown Clay	1	1
Bleu Brick Yard Clay		2
Lake Albany - 152' Depth		1
Lake Albany - 83' Depth	1	1
Lake Albany - H_2O_2 Treated 83' Depth		1

In addition to the above, nine (9) thermograms were obtained for Alumina versus Alumina, as follows:

Oven Dried (for 24 hours at 50°C) vs. Oven Dried (24 hrs. at 50°C)	6
Dried at 300°C-400°C vs. Oven dry (24 hrs. at 50°C)	3

INTRODUCTION

The differential thermal method of analysis of soil samples has as its purpose the identification of the minerals (clay minerals or other minerals of "clay-size" particles) present in the soil, and a determination of the relative abundance of these minerals. The method consists of heating at a uniform rate a sample of the soil and a similar sample of an inert substance from room temperature to over 1000°C. During this heating process, changes occur in the structure of the soil particles and this results in the release or imbibition of heat. Since there are no structural changes in the inert material, a measure of the changes in the soil is reflected in the difference in temperature between the soil and inert substance samples created by the thermal reaction of the sample. This temperature difference is measured by a differential thermocouple. Each mineral has a characteristic curve of thermal change (i.e., difference in temperature between soil and inert material) versus temperature.

Identification of the minerals present in a sample of soil is accomplished by comparing the differential thermal curve, or thermogram, of the soil unknown with curves of known pure minerals. More detailed discussion of the theoretical basis for differential thermal analysis can be found in theses presented by Merritt and White in 1951 (1), and Hoskins and Hudson in 1950 (2).

The reader is referred to the thesis by Merritt and [illegible] [illegible], and also to the one by [illegible] [illegible], for a complete description of instrumentation used in differential thermal analysis. Briefly, the equipment consists of a horizontal electric furnace, the heating rate of which is automatically controlled by a variable transformer, which is regulated by a potentiometer pyrometer, a self-balancing recording potentiometer, to record the internal temperature of the sample and the difference between the temperature of the sample and inert standard material, and a nickel sample holder, with chromel-alumel thermocouples. To this basic instrument set-up, the authors added certain accessories to increase the consistency of results and the productivity of the equipment.

Thermocouple Tester

It was noticed that frequently, one of the thermocouples was broken in some location not visible to the operator. In such a case, it was only after the sample holder had been loaded and the actual test run begun that the operator discovered the broken thermocouple; it was necessary then to discontinue the run and reload the sample. Each such occurrence represented a considerable loss of productivity because of the time required in removing and loading a new sample. A tester was constructed therefore, for the purpose of

testing the thermocouples of each sample holder before it was loaded for each run. This tester consists of a small D. C. ammeter which can be connected in succession through a multiple position switch to each of the three thermocouples in the sample holder. A common 1.5 volt flashlight battery supplies the test current. This tester has been permanently added to the equipment available for use in differential thermal analysis of clay minerals.

SAMPLE COMPACTING RAM

The theoretical requirements that must be considered in differential thermal testing will be discussed later. However, it is important to note here that among these requirements is the necessity that the mass, specific heat, and conductivity of the sample be equal to those of the inert standard. These properties are clearly dependent on the particle size and shape, void ratio, moisture content, and specific gravity of both the sample and the inert standard. Particle size, moisture content and the relation between specific gravities are controlled by the test procedure but the void ratio is normally permitted to vary considerably since compaction of material in the sample holder cells is accomplished only by vibrating the holder, or finger tapping. To improve the consistency of results, a ram was made to compact the

sample and inert materials into the sample holder. This ram fits snugly into the sample holder cells, and simply compacts the material under the weight of the ram. A uniform pressure of 2.5 pounds per square inch is applied to the materials by the ram.

EQUIPMENT

DIFFERENTIAL TEMPERATURE SCALE OVERLAY

The recording potentiometer produces an almost continuous plot of sample temperature difference between sample and inert standard. Rough comparisons of the thermal characteristics of the various materials may be made on the basis of these plots but the plots are inconveniently large and, for reasons to be discussed later, not perfectly comparable without modification. For this reason it is necessary to reduce each plot to a corrected curve of differential temperature (expressed in millivolts induced in the differential thermocouple) versus temperature of the sample. Because the location of the zero millivolt line shifts from run to run it is impractical to print the differential temperature scale on the record paper and the operator must by some other means measure the magnitude of the induced voltage. The authors have found that the most satisfactory method of doing this is to superimpose a transparent overlay, or template, of the voltage scale over the potentiometer record. A scale is thus provided for both sets of data which must be read from the instrument record. The template has been contributed to the equipment of the laboratory.

1750-WATT FURNACE

In accordance with the recommendations of Merritt and White (1) one of the 1000 watt furnaces was rebuilt

with a 1750 watt heating element. In view of the difficulties experienced by Merritt and White one furnace was not converted, however, in order to provide a check on the performance of the two 1750 watt furnaces. As predicted by Merritt and White, the difficulties with the 1750 watt element disappeared after a number of test runs and consequently the remaining 1000 watt furnace has been converted.

Thermocouples

Merritt and White employed oxy-acetylene welding in preparation of thermocouples--apparently because of previous unsatisfactory experience with electrical resistance welding. Oxy-acetylene welding produces a large heat at the point of connection which decreases the sensitivity of the thermocouples and the authors found that many gas-welded thermocouples were not truly fused. More satisfactory thermocouples were produced by using an electric arc for fusing the ends of the wires together. The two thermocouple wires were used as one electrode and a shallow layer of mercury submerged in a quenching oil, as the other electrode.

The spark induced by making a near contact between the electrodes under the surface of the oil fused the thermocouple wires. A 125 volt, D.C. current source was used, with approximately 4 ohms of

resistance inserted in the circuit. This type of welding of the thermocouples produced very satisfactory small beads at the joint.

PROCEDURE

In the differential thermal procedure, the temperature of an inert substance is taken as the temperature of the environment of the thermally active sample. This fact, together with the observations made under theory, permit the listing of certain theoretical requirements which must be taken into consideration in differential thermal analysis. The more important of these requirements, as listed by Lambe (5), are as follows:

1. The mass, specific heat, and conductivity of the sample must be equal to those of the inert material.
2. The beads of the thermocouples must be located at the centers of the sample and the inert standard, or as near the same relative position as possible.
3. The inert material must be truly inert.
4. The sample and the inert material must be heated in an infinite thermal reservoir.
5. The reservoir, or holder, must be symmetrical with respect to the sample and inert cells.
6. The particle size should be small to obtain as great specific surface as practicable.

In the light of these theoretical requirements, in general, the procedures as recommended by Merritt and

White (1), were followed in the investigations. Certain changes were made in the recommended procedure, because of the equipment changes made by the authors (see Equipment).

The procedure followed in this work, was as follows:

GRAIN SIZE

All samples used in the investigations were made up of clay particles passed through a 200 mesh sieve. This size was used in the interest of uniformity, and to remove particles of larger than large clay sizes.

In addition, the 200-pan grain size was used to obtain as large a specific surface as practicable, and to increase the surfaces of contact between the particles, which in turn increased the thermal conductivity of the sample.

PRETREATMENT

It appears desirable to maintain the whole differential thermal analysis procedure as simple and as standard as possible. In view of this requirement, no pretreatment other than oven drying at 50°C was used on any of the samples used in the tests to arrive at standard curves, and to determine the effects of admixtures of inert materials. In the attempts to identify the unknown clay samples, however, the Lake Albany Clays

were treated with H_2O_2 to remove the organic matter which appeared to be present in the initial test runs on these materials.

Subjecting the clay materials to be tested to relative humidities of 50 percent, as recommended by Lambe (5), would seem to introduce several possible errors which would be difficult to overcome. Specifically, these probable errors appear to be in the amount of time necessary for a clay mass to reach moisture equilibrium under the known humidity. Overcoming these probable errors seems not only a difficult task, but would be time consuming, as well, which appears unjustifiable.

It was deemed unnecessary, also, to use other pretreatment methods, except in the specific cases, mentioned, since the thermograms in all but one case, exhibited little or no evidence of organic or other foreign matter.

HEATING RATE

The heating rates recommended by other investigators, Lambe, Hauth and Davidson, and others, vary from 10 to 15°C per minute (600 to 900°C per hour), with most work being done at 12.5°C per minute (750°C per hour). Merritt and White (1) however, have determined that heating rates of

1023°C per hour for the 1750 watt furnaces, and 500°C per hour for the 1000 watt furnace were the best heating rates to be used with the equipment utilized by the authors. For this reason, the heating rates as recommended by Merritt and White were used throughout our work.

INERT MATERIAL

The most commonly used inert standard material, and the standard used in these investigations, is calcined aluminum hydroxide, or alumina (gamma aluminum oxide). After predrying the alumina at temperatures of 300 to 400°C, the material was kept dry by placing it in the oven for future use. The alumina thus was kept in the oven for periods varying from 24 hours to several weeks.

Lambe (5) has stated that the alumina picks up moisture very readily from the atmosphere, and for this reason must be preheated to at least 250°C, and then cooled, within a few hours previous to each test run. He further states that if this were not done, the removal of adsorbed water on the supposedly inert material would vitiate the deflections of the thermograms caused by the removal of adsorbed water from the test sample. The inert material thus pretreated, was used in the differential thermal analysis of sample materials

pretreated at 50 percent relative humidity.

The authors, to determine whether or not the pretreatment recommended by Lambe was required, made several test runs of alumina versus alumina, both cells of the holder filled with alumina oven dried at 50°C for several days after initial preheating at 300 to 400°C, and then with one cell of this same material versus a cell of alumina just cooled from the 300 to 400°C temperature. The results are recorded under Conclusions.

The alumina used in these investigations was ground to pass a 200 mesh sieve, to maintain the thermal conductivity of the alumina and the sample as nearly equal as possible.

WEIGHT OF SAMPLE

The samples used in the test runs were of known weight. Both the sample and the alumina were weighed to the nearest 0.0001 gram. As recommended by Merritt and White, the sample and the inert material were equal in weight in most tests. In the cases of the small weights, sufficient alumina was added to the sample cell and the inert cell, to produce enough mass to cover and surround the thermocouple beads. Equal amounts of the alumina were added to each cell of the holder, to prevent too great a displacement

of the base line. The alumina and the sample were thoroughly mixed, to provide a homogenous mass in the sample cell.

COMPACTION OF INERT MATERIAL AND SAMPLE

As has been noted under Equipment, a ram was used to compact the sample and alumina in an attempt to obtain uniform densities. In addition to resting the ram on the materials for approximately ten seconds, the holder was tapped vigorously on a hard, firm surface several times, to insure that the thermocouples were thoroughly imbedded in both the alumina and the sample.

THERMOCOUPLES

Prior to filling the cells of the sample holder, a check was made with the circuit tester (see Equipment) to verify the fact that all the circuits in the sample holder were in working order.

In addition, checks were made to see that the thermocouple beads were located in the centers of the cells, or in the same relative positions with respect to both sample and alumina.

REMARKS

By the steps in the procedure recorded above, the authors attempted to conform to the theoretical requirements as stated by Lambe (5).

PROCEDURE

The only requirements noted by Lambe and not covered above in the outline of procedure used by the authors are requirements 3 and 4. Requirement 3, that the inert material must be truly inert, will be discussed later under Observations.

Requirement 4, concerning the infinite thermal reservoir, was assumed to be complied with, since the weights of the samples used were comparatively insignificant with respect to the weight of the sample holder. Appendix III contains calculations which show that to raise a 0.70 gram sample of clay 10° C. requires 1.54 calories and that this quantity of heat is sufficient to change the temperature of the sample holder only 0.06° C. In other words an endothermic reaction sufficient to cause a 10° C. difference in temperature between sample and standard would cool the sample holder only 0.06° C. if there were no heat input from the furnace. This, plus the fact that the hot furnace is itself a large thermal reservoir indicates that requirement 4 is adequately fulfilled.

[illegible]

After completion of a test run, six hours or more were required for the furnace to cool to room temperature. It was found impossible, therefore, to complete more than one test during a normal

work day with the three furnaces available. Some decrease in the time required for cooling the furnace was obtained by using a small laboratory air compressor to blow a stream of air into the open furnace. The air was bubbled through a water container to remove any oil that it might have picked up in the compressor. Even this arrangement did not cool the furnaces quickly enough to permit continuous operation of the recording equipment. More rapid cooling of the furnaces might decrease the life of the heating elements so it appears that maximum productivity of the apparatus can be obtained only by adding another furnace.

INVESTIGATIONS AND OBSERVATIONS

HYDRATION OF ALUMINA

A number of test runs were made to determine the degree to which alumina, the inert standard used in all the tests, became hydrated through adsorption of atmospheric moisture. In these tests alumina previously heated and then stored for several days in an electric oven at 50°C was used as the test material and alumina heated to between 300 and 400°C just before the test was used as the inert standard. The thermograms for these curves were straight lines with no endothermic peaks to indicate loss of adsorbed water. Moreover, reheat tests of the same material made as soon after the original tests as the sample holder and sample could be cooled gave thermograms which coincided exactly with the original test thermograms. Since it seems unlikely that these samples while cooling rapidly from 1100°C to room temperature could adsorb much moisture from the atmosphere of a heated laboratory, this coincidence of initial and reheat thermograms is accepted as evidence that the original test did not drive off moisture at a uniform rate throughout the heating range.

It is important to note that the coincidence of the differential thermal curves from initial and reheat tests of alumina prove that this material satisfies the third theoretical requirement of differential thermal tests.

INVESTIGATIONS AND OBSERVATIONS

EFFECT ON THERMOGRAMS OF MIXING INERT MATERIAL WITH THE INITIAL SAMPLE

It has been stated by Merritt and White (1) that the thermal activity of a given sample of pure mineral (as measured either by the area under the differential thermal curve or by the amplitude of the curve) is proportional to the mass of the sample. Quantitative analysis of the constitution of an unknown material is made possible therefore by comparing the thermogram of the unknown with thermograms prepared for known weights of known pure minerals. If the amplitude of the unknown material's thermogram at the temperature of a characteristic reaction of a known pure mineral matches the amplitude of a thermogram for "x" grams of the pure mineral, it is assumed that "x" grams of the pure mineral are present in the sample. A set of standard curves for known weights of pure minerals are essential, therefore, to quantitative analysis by the differential thermal method.

The cells of the sample holders used in these tests hold a maximum of 0.8 grams of clay sample and a minimum of 0.6 grams is necessary to cover the thermocouples. It is necessary, therefore, to increase the volume of samples smaller than 0.6 grams if standard curves for weights less than 0.6 grams are to be obtained. A considerable number of tests were made, to determine the effect on the thermal reactions of the

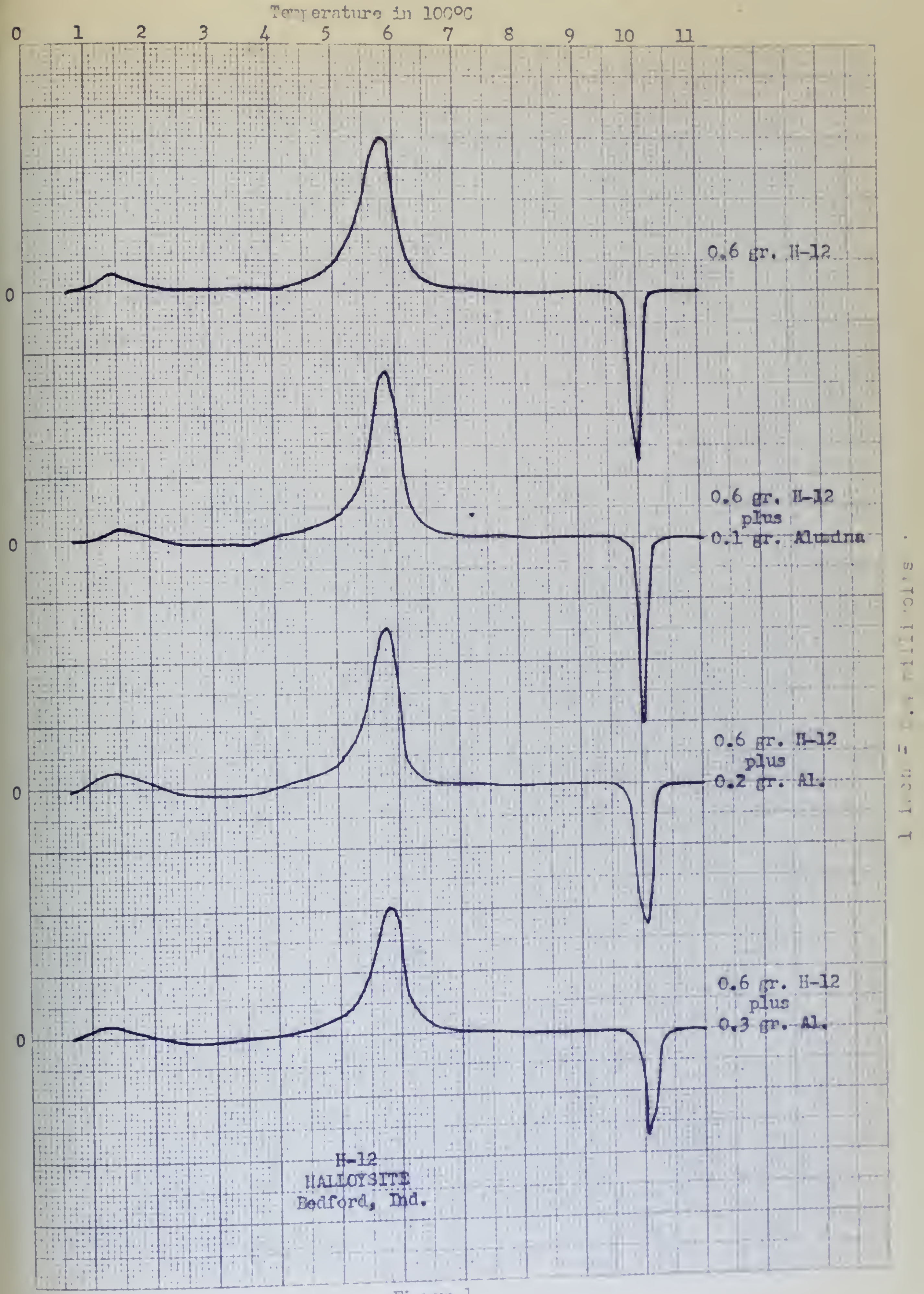

Temperature in 100°C
0
1
2
3
4
5
6
7
8
9
10
11
0
0.6 gr. H-12
0
0.6 gr. H-12
plus
0.1 gr. Alumina
0
0.6 gr. H-12
plus
0.2 gr. Al.
0
0.6 gr. H-12
plus
0.3 gr. Al.
H-12
HALLOYSITE
Bedford, Ind.
1 inch = [illegible] millivolts.

Figure 1

sample of mixing alumina with the pure clay mineral. American Petroleum Institute standard Halloysite H-12 was used for these tests because of the large, well defined reactions of this material. Figure 1 shows thermograms for a 0.6000 gram sample of Halloysite H-12 and for the same weight of H-12 mixed with varying weights of alumina.

LOCATION OF THE [illegible] BASE LINE

Theoretical analysis of the heat balance at the center of the sample as noted by Merritt and White (1) has demonstrated that the area under the differential temperature curve is proportional to the mass of the reacting material. Measurement or calculation of the area under the curve is complicated by the irregular shape of the curve. Quantitative analysis of a material on the basis of the ratio of the area under the curve of the material to the area under the curves of pure minerals is further complicated by the fact that different portions of the curve of a composite material are characteristic of the curves of different pure minerals. It becomes necessary, therefore, to decide which portions of the curve are to be compared with each standard curve and to set arbitrary boundaries which delineate the separate portions. Most investigators have sought to eliminate the tedious work involved in determination of the area under the curve and at the same time

minimize the errors introduced by assumption of arbitrary boundaries of the area by assuming that all the curves of a given material have the same shape and that the area under a characteristic peak of the curve is proportional to the amplitude of the peak.

The simplest base from which to measure the amplitude of the various peaks is, of course, the zero millivolt line. However, if a test run is made with an inert material in both cells of the sample holder it will usually be found that the thermogram, though it is a straight line and shows no thermal reactions in the materials, does not coincide with the zero millivolt line. As was pointed out by Merritt and White (1), two factors--the relative thermal conductivities and relative specific heats of the sample and standard materials--are responsible for this displacement of the actual base line which must be used for measurement of thermal reactions. Merritt and White correctly concluded that the location of this displaced base line is entirely a function of the materials (specifically the state of compaction, volume of materials, grain size, and other factors governing the thermal conductivity of the materials), and that, since the magnitudes of the thermal reactions as measured from the displaced base line are not affected by the displacement, the evaluation of a

differential temperature curve for quantitative analysis should be made with respect to the displaced base line. Like other investigators, Merritt and White experienced considerable difficulty in locating the displaced base line or the assumption that the displaced base line is a horizontal (that is, parallel to the zero millivolt line) line tangent to the thermogram at a temperature where the material is known to be undergoing no reaction. It will be shown that this assumption is in error and a more accurate method of locating the displaced base line will be described.

It was noticed that the straight line thermogram obtained by heating alumina in both cells is not ordinarily parallel to the zero millivolt line. The angularity between the displaced base line and the zero millivolt line is a result of changes in the thermal conductivity and/or specific heat of the material as it is heated. Apparently the angularity is a function of the conditions within the sample and not a characteristic of the material because it has been observed that the displaced base line may slope in either direction. Excepting the few minerals which exhibit reversible reactions, the thermograms obtained by reheating a sample previously calcined or used in a differential thermal test is a straight line similar to that obtained for alumina and like the thermograms

for alumina has been observed to normally be displaced from the zero millivolt line and lie at an angle to it. Since the reheat thermogram of a reheated clay sample is a straight line it may be assumed that the clay loses its thermal activity during the initial heating to 1100°C. Any displacement of the reheat thermogram from the zero millivolt line represents a difference in the thermal gradients within the sample and standard materials, but only to differences in the heat transfer properties of the materials. If now, the sample used in obtaining the thermogram for a clay mineral is cooled and then reheated without disturbing the material in either the test or standard cells, the reheat curve will give a measure of the degree to which displacement of the base line effected the amplitude, from the zero millivolt line, of the thermogram. If the reheat curve is plotted on the initial thermogram it will be tangent to the initial thermogram in those temperature ranges in which the material does not undergo thermal reaction. The reheat curve is, therefore, the base line from which the true amplitude of the deflections of the thermogram should be measured. It should be noted that the base line is, therefore, not necessarily parallel to the zero millivolt line.

It is not desirable to reduce the productivity of the apparatus in terms of the number of samples

analyzed, by reheating each sample to locate the displaced base line, and, fortunately, this is not always necessary. Obviously if a number of tests are to be made on the same material it will suffice to reheat only a few samples in order to learn which portions of the thermogram of that material lie on the displaced base line. All other thermograms of the material can be analyzed by drawing the displaced base line through those portions of the thermograms proved to be inactive.

POSSIBILITY OF A VARIABLE BASE LINE

Kerr, Kulp, and Hamilton (8), mentioned the possibility that decomposition of a sample during the heating might so alter the relative thermal conductivity and specific heats of the sample and inert standard as to cause a shift in the base line. The authors believe that there also exists the possibility that changes in these relative properties may cause the base line to become a curved line rather than simply two offset segments of a straight line. The authors found no evidence to suggest that this shift occured in the tests reported herein. It was noticed, however, that the tests gave more widely scattered results in the lower temperature ranges and generally gave more consistent readings above 200°C. Similarly, many of the reheat curves deviated from a straight line only below 200-300°C. Time did not permit further tests to determine whether these difficulties resulted from a

shift in the base line or merely a continuation of the difficulties reported by Merritt and White in obtaining consistent differential thermal curves with the 1750 watt furnaces.

THERMOGRAMS FOR CERTAIN STANDARD CLAY MINERALS

Differential thermal curves are presented for five of the minerals now accepted in this country (see reference 8) as standard reference clay minerals. These curves have been checked and found to coincide in general shape with curves derived by others (see references 5, 6, and 8) for the same materials. Detailed checking of these curves with published curves has not been possible because of some unexplained reluctance of other investigators to publish numerical values or scales for their curves. So many variables (grain size, heating rate, pretreatment of sample, etc) affect the magnitude of the deflections of the differential thermal curve that practically, it is necessary to develop standard curves for each apparatus set up, hence it is considered that the primary value of published curves is for shape reference only. The curves presented herein are applicable as standards for quantitative analysis under the following conditions:

> The curves are for tests of samples all grains of which pass a 200 mesh sieve. Pretreatment, heating rate, degree of compaction have been

described; in all cases the weight of inert material was equal to the weight of material in the sample cell. Ordinates of the curves are measured from the displaced base line located as described above. Thermocurves of unknown materials should be obtained with the same apparatus as the standard curves used in the analysis.

Figure 4, a curve of reaction versus weight of halloysite present in the sample, presents the data of Figure 3 in a form thought to be more generally applicable to quantitative differential thermal analysis.

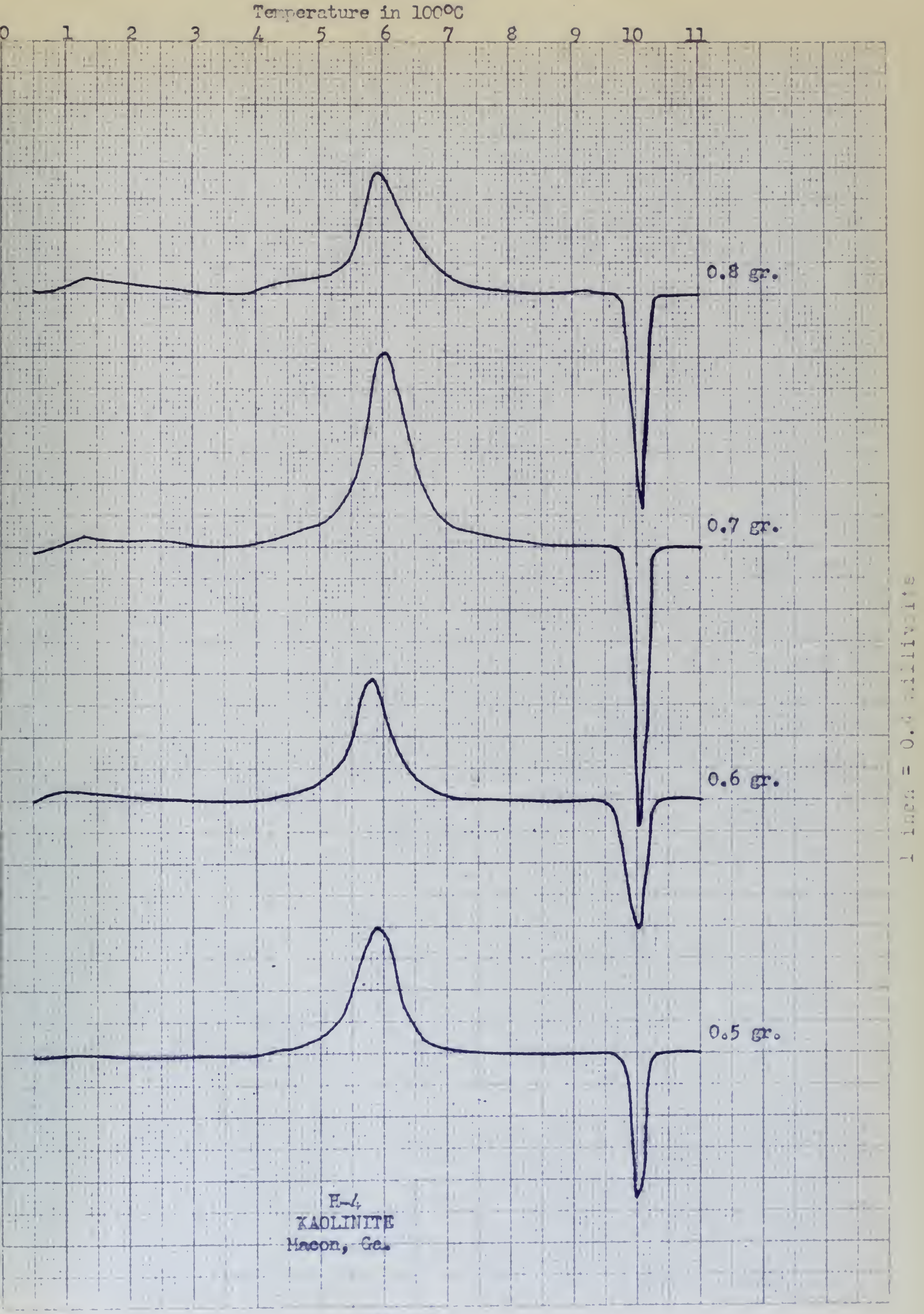
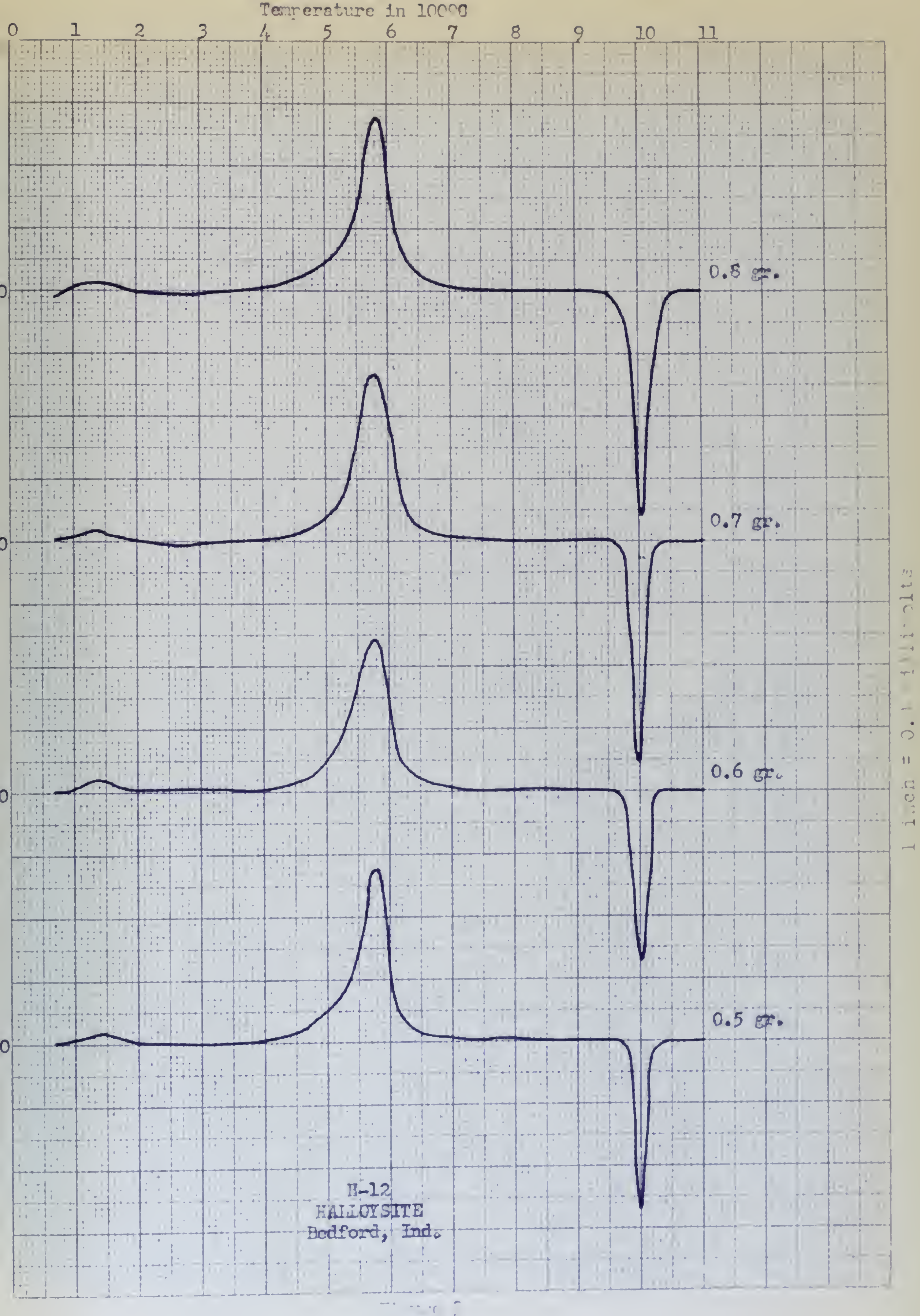

Temperature in 100°C
0
1
2
3
4
5
6
7
8
9
10
11
0.8 gr.
0.7 gr.
0.6 gr.
0.5 gr.
1 inch = 0.4 millivolts
K-4
KAOLINITE
Macon, Ga.

Figure 2



H-12
HALLOYSITE
Bedford, Ind.

Figure [illegible]

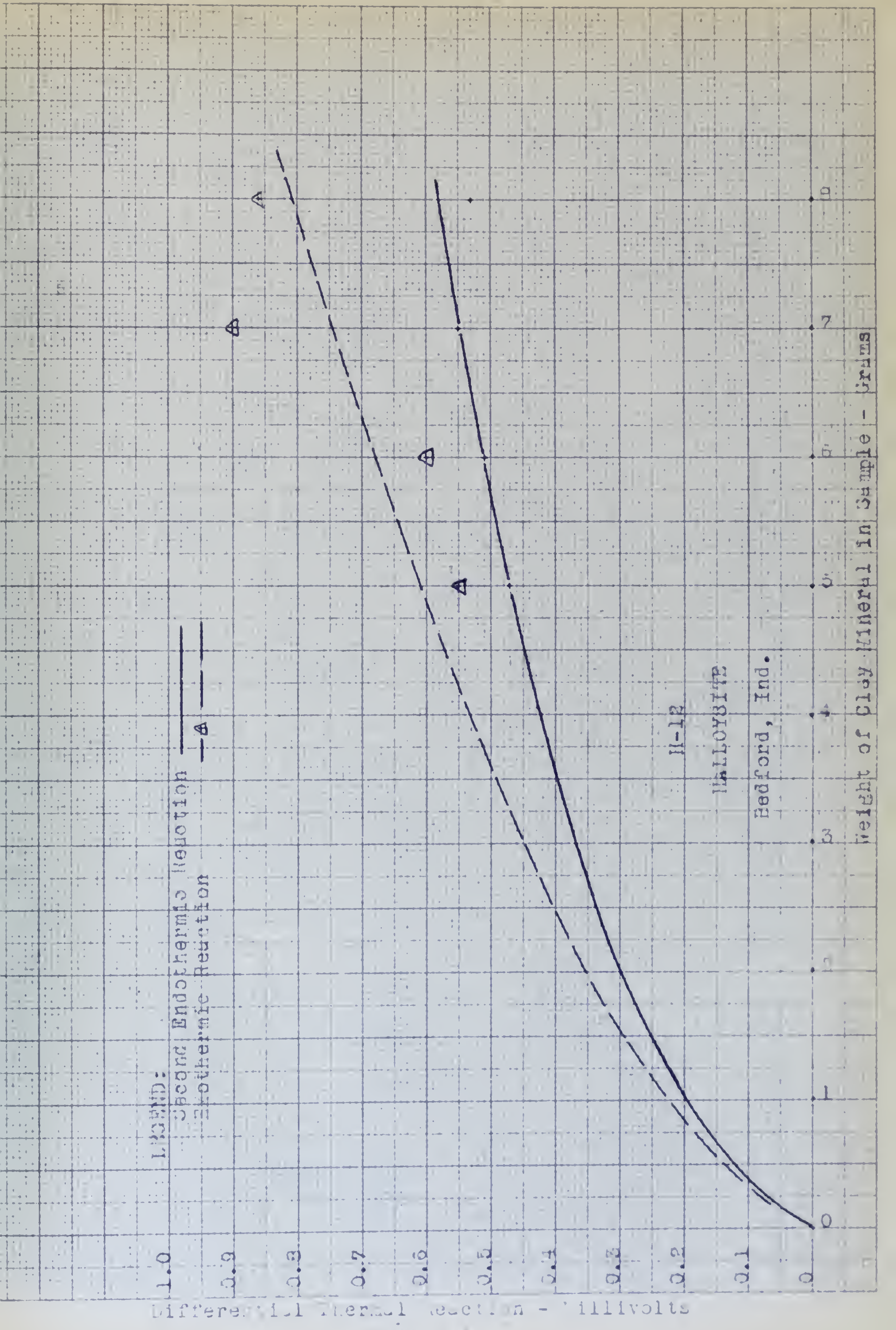
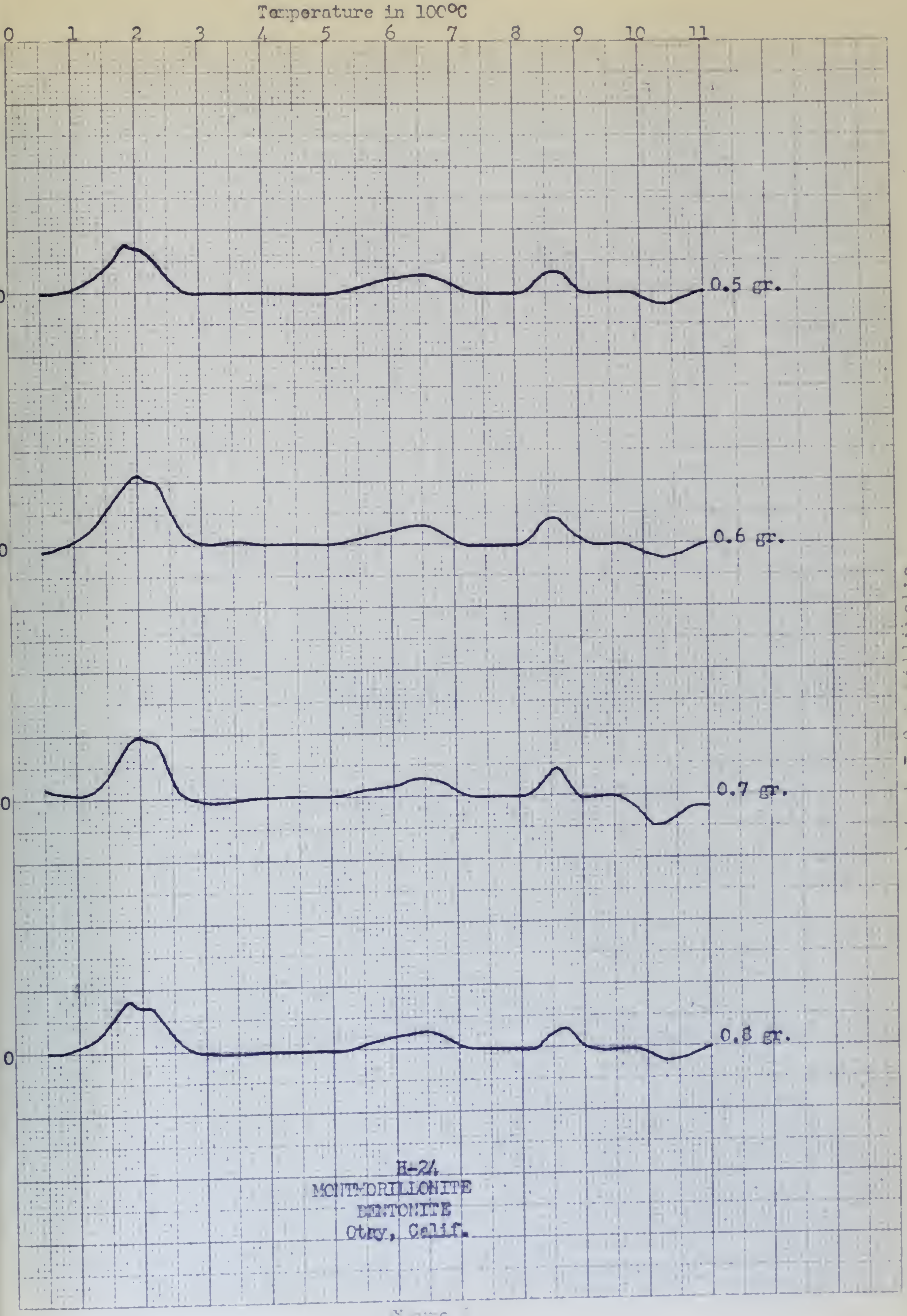
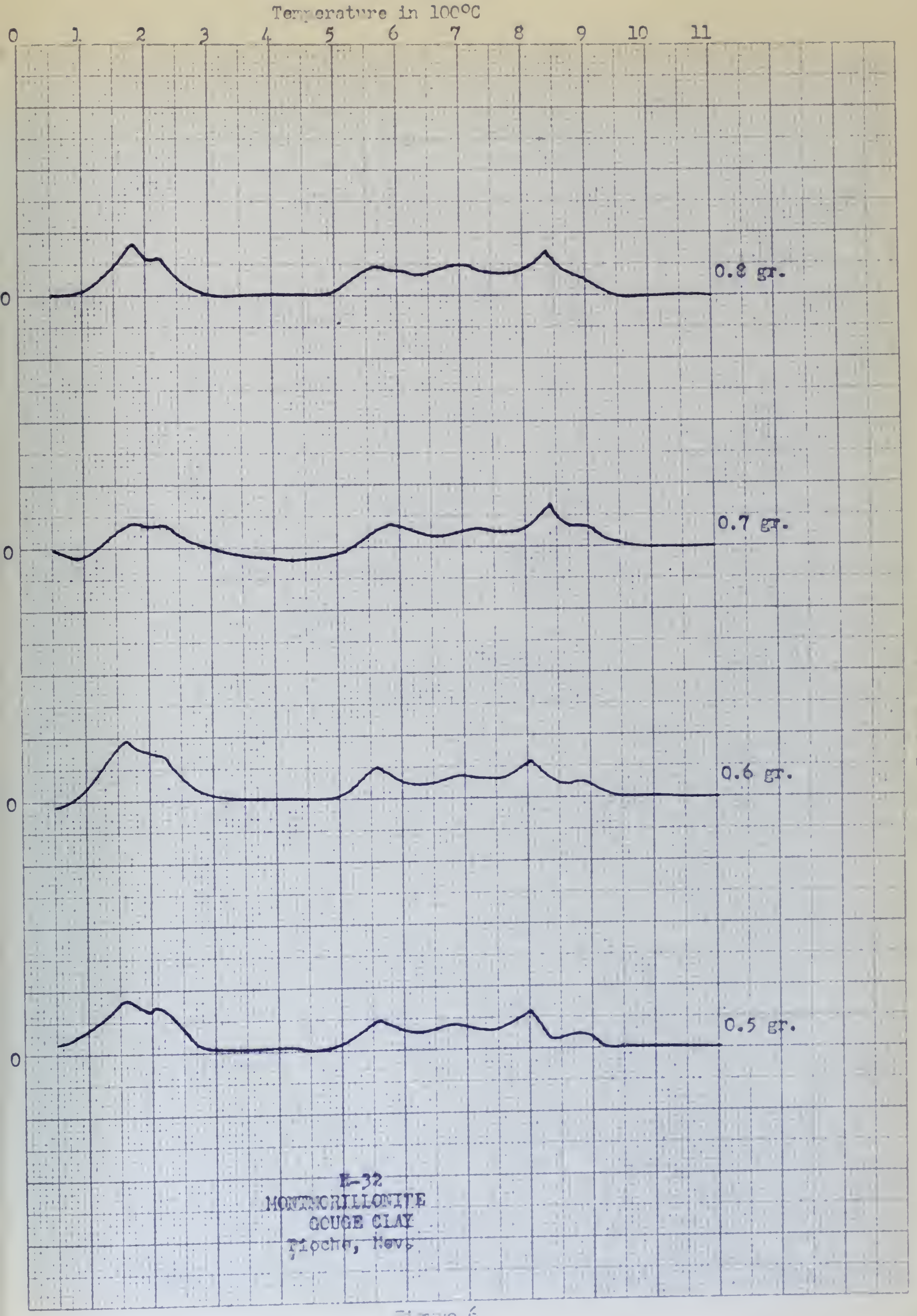

LEGEND:
Second Endothermic Reaction
Exothermic Reaction
H-12
HALLOYSITE
Bedford, Ind.
Weight of Clay Mineral in Sample - Grams
0
1
2
3
4
5
6
7
8
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Differential Thermal Reaction - Millivolts

Figure 4



H-24
MONTMORILLONITE
BENTONITE
Otay, Calif.



E-32
MONTMORILLONITE
GOUGE CLAY
Pioche, Nev.

Figure 6

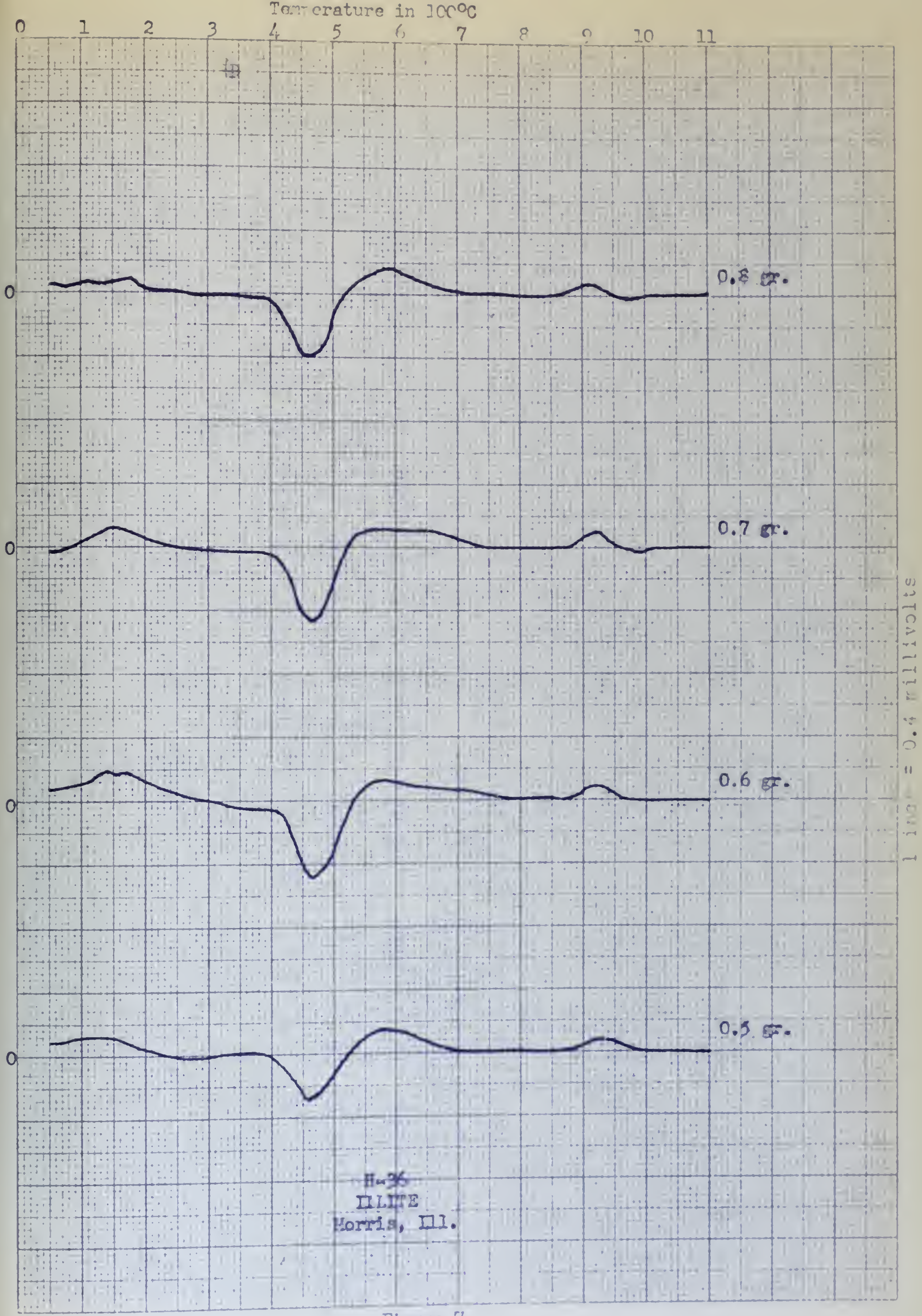

Temperature in 100°C
0
1
2
3
4
5
6
7
8
9
10
11
0
0.8 gr.
0
0.7 gr.
0
0.6 gr.
0
0.5 gr.
1 inch = 0.4 millivolts
H-36
ILLITE
Morris, Ill.

Figure 7

INVESTIGATIONS AND OBSERVATIONS

ANALYSIS OF CERTAIN UNKNOWN CLAYS

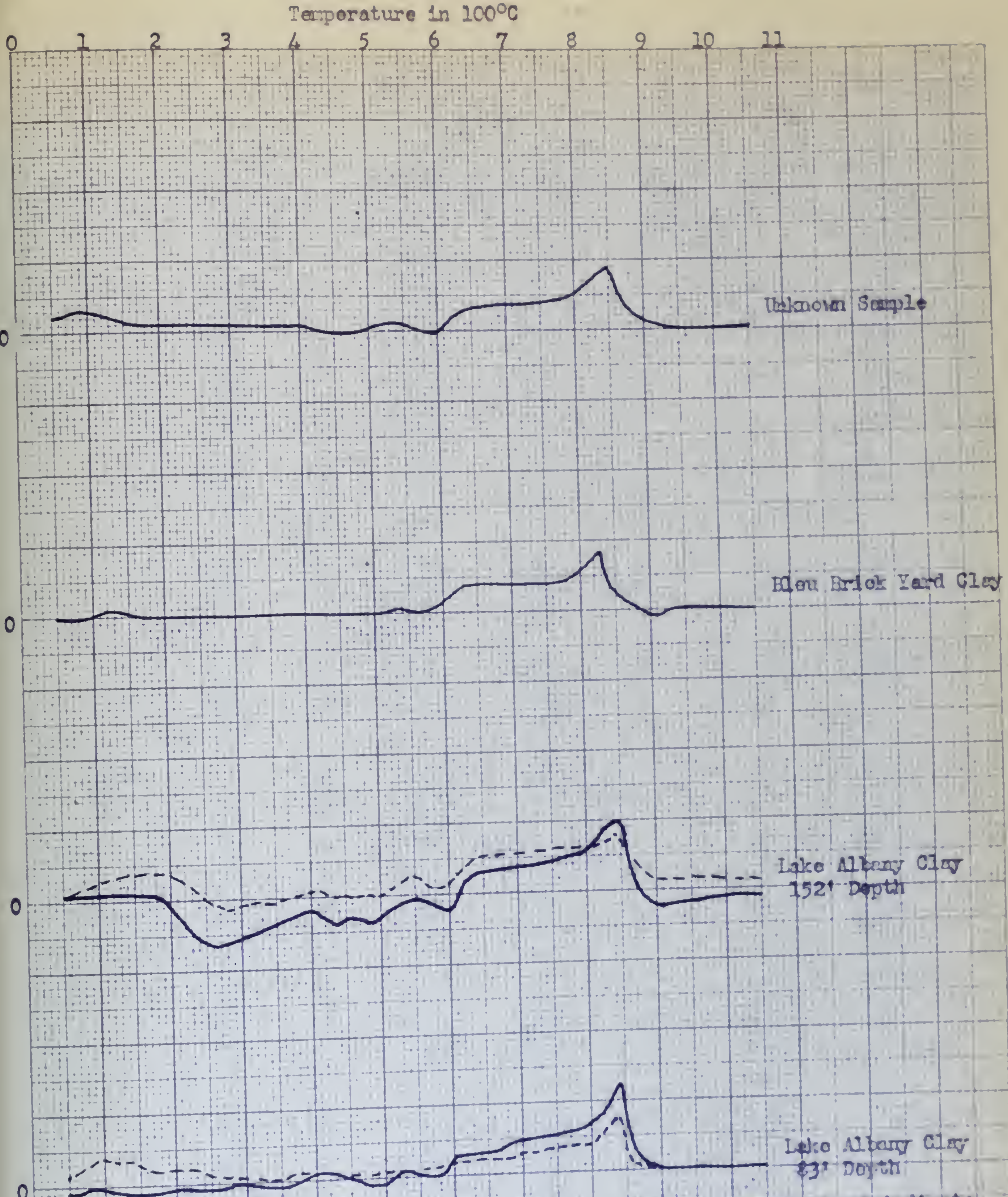
Thermograms were produced for four clay soils provided by Professor Kilcawley, for analysis. It will be seen in Figure 6, that the composition of all four clays appears to be quite similar. The thermograms resemble those for montmorillonite and appear to be influenced by the presence of organic matter. The presence of organic matter in the two Lake Albany Clays is well established by the fact that treating the clays with hydrogen peroxide to digest the organic matter greatly modified the thermogram. The thermogram for the treated samples matches even more closely the curves for montmorillonite.

REVERSIBLE REACTIONS

A considerable number of reheating tests were made for the purpose of locating the displaced base lines of each material tested. The time lapse between initial heating and reheating varied from one to several hours, but in no instance was a reversible reaction observed in any of the clay minerals tested. The well known reversible endothermic reaction of quartz at 573°C was observed in two tests of quartz sands tested.

INHERENT INACCURACIES IN THE DIFFERENTIAL THERMAL METHOD

Table I, is a tabulation of the observations of a number of tests of the critical values (i.e. magnitude of deflection and temperature at which peak deflection



Dashed lines indicate thermograms of same material after treating with H_2O_2

THERMOGRAMS OF UNKNOWN CLAY SAMPLES

TABLE I

OBSERVED PEAK REACTIONS OF H-12 HALLOYSITE

	SECOND ENDOTHERMIC			EXOTHERMIC			
Run No.	Temp. °C	Defl. mv.	Residual in Defl.	Temp. °C	Defl. mv.	Residual in Defl.	Remarks
34	574	.32	-0.19	1020	.41	-0.19	0.6 gr.
35	589	.80	+0.29	1010	.98	+0.38	"
36	579	.69	+0.18	1019	.90	+0.30	"
37	570	.47	-0.04	1009	.58	-0.02	"
38	580	.65	+0.14	997	.62	+0.02	"
49	565	.31	-0.20	1010	.48	-0.12	"
39	578	.45	-0.06	1015	.58	-0.02	0.6gr+0.1 al.
40	590	.83	+0.32	1017	.83	+0.23	
41	580	.43	-0.08	1014	.48	-0.12	
42	577	.51	0.00	1005	.54	-0.06	0.6+0.2 al. gr.
44	585	.55	+0.04	1018	.68	+0.08	
48	578	.52	+0.01	1020	.66	+0.06	
45	562	.47	-0.04	1015	.56	-0.04	0.6gr.+0.3 al.
46	580	.51	0.00	1019	.55	-0.05	
47	579	.19	-0.32	999	.23	-0.37	
53	585	.43	-0.08	1020	.54	-0.06	
total		8.13	1.99		9.62	2.12	
average	580	.51	.12	1013	.60	.13	
63	589	.56	+.03	1012	.89	+.03	.8 gr.
64	583	.61	+.08	1005	1.11	+.25	
65	575	.42	-.11	1021	.58	-.28	
total	1747	1.59	.22	3038	2.58	.56	
average	582	.53	.07	1013	.86	.19	
52	579	.53	-.02	1005	1.08	+.18	.7 gr.
54	584	.60	+.05	1010	.94	+.04	
56	589	.52	-.03	1000	.68	-.22	
total	1752	1.65	.10	3015	2.70	.44	
average	584	.55	.03	1005	.90	.15	
56	560	.24	-.23	1000	.30	-.25	.5 gr.
57	610	.44	-.03	1080	.60	+.05	
61	578	.51	+.04	1000	.58	+.03	
72	575	.60	+.13	1010	.68	+.13	
74	580	.58	+.11	1015	.61	+.06	
total	2903	2.37	.54	5105	2.77	.52	
average	581	.47	.11	1021	.55	.10	

TABLE II

ERROR IN OBSERVATIONS OF PEAK REACTIONS OF H-12 HALLOYSITE

	2'nd Endothermic Reaction				Exothermic Reaction			
Wt. Mtl.	Most probable Defl. Mv.	a.d.	A.D.	ΔDefl.	Most probable Defl. Mv.	a.d.	A.D.	ΔDefl.
.5	.47	.12	.05	+.04	.55	.12	.05	+.05
.6	.51	.13	.03	+.04	.60	.14	.03	+.30
.7	.55	.04	.02	-.02	.90	.18	.10	-.04
.8	.53	.09	.05		.85	.23	.13	

occurs) of two characteristic reactions of Halloysite API Standard H-12. The tests are grouped into a number of series, each series including all tests of a given weight of the material. It will be noted that the observed values in each series are widely scattered; this despite every effort to standardize the procedure and minimize accidental errors. These data were examined by the usual methods of statistics (see reference 7) for the purpose of determining which observations, if any, should be rejected and to estimate the accuracy of the values.

The mean error in a single reading is listed in Table IV, for each of the series of tests (see Appendix II for calculations). For example, the mean error in the individual tests of 0.6 gram samples was 0.13 mv. for the second endothermic reaction and 0.14 mv. for the exothermic reaction. These errors represent 25.5 percent and 23.4 percent respectively of the most probable values for these reactions. This cannot be taken as an indication of the accuracy of the data obtained but it does indicate that the precision of the differential thermal method is not favorable to quantitative analysis. A mean error in a single reading of 0.13 mv. means simply that if another test were made it could be expected that on the average the measured reaction would vary from the mean reaction by 0.13 millivolts. An additional test of 0.6 grams of

H-12 would be expected, therefore, to give a value of either 0.35 millivolts or 0.64 millivolts for the second endothermic reaction. It may be seen on figure 4 that these would indicate the presence of either 0.315 grams or 0.975 grams of the material, an error in weight of either 47.5% or 62.5%. Perhaps the significance of the lack of precision may be better understood in another way. The authors have found that for most clays, a sample weighing 0.7 grams is the most suitable size for testing in the present apparatus. Suppose that the sample tested contained 0.6000 grams of H-12 mixed with 0.1000 grams of an inert material. The sample therefore would have consisted of 85.7% of clay mineral and 14.3% of inert matter. If the reaction measured in a single test was less than the mean by the amount of the average deviation, the sample would appear to be composed of 45% of clay mineral and 55% inert matter; if the reaction measured in a single test exceeded the mean by the amount of the average deviation, the sample would appear to contain 0.975 grams of clay mineral or 139% of the known weight of the sample. A single reading could not be trusted to give a quantitative analysis more accurate than merely placing the clay content within the range of 45 to 139%.

To overcome the lack of definition inherent in an analysis based on a single reading it is necessary to run a number of tests and average the results. Table II lists the average deviation of the mean values determined by the authors in their tests of H-12.

Comparison of these deviations with the rate of change in amplitude values with increasing sample weight indicate that the accuracy of the value derived by averaging several tests was not sufficient to distinguish a change in sample weight of 0.1 grams. Assuming a sample composed of [illegible] grams of L-12 and [illegible] grams of inert material as before, the error in the mean value would not permit estimating the composition of the sample more accurately than saying that it contained from [illegible] percent to 64 percent of L-12. To estimate the composition within 5 percent of the true 35.7 percent represented by the 0.6 grams of L-12 contained the sample would require [illegible] tests (assuming that the mean error in a single reading remained at 0.15 millivolts).

As the description indicates, the apparatus and procedure used in these tests appears to satisfy the requirements for successful application of the differential thermal analysis. Every precaution was taken to insure that the tests were conducted with great care and precision. There remains, therefore, no explanation for the lack of precision and the apparently large errors in the data obtained. It appears that lack of precision is inherent in the process and must be accepted as a limitation of the applicability of the differential thermal analysis.

CONCLUSIONS

In consideration of the observations made during the tests, the following conclusions are drawn.

1. If there is reason to believe that the alumina to be used in differential thermal tests is not dry, it would be desirable, before placing it in the test sample holder, to heat the alumina to several hundred degrees Centigrade to drive off the adsorbed water. If the alumina is known to be dry, simply storing it with the dry clay minerals in an oven at 50°C is sufficient treatment to insure against introduction of error into the test procedure. The authors find no reason to follow Lambe's (5) recommendation that the alumina be heated to several hundred degrees just prior to each test run.
2. Deflections of the thermograms are a function of the mass of active mineral tested and are not influenced by the presence of inert materials mixed with the active minerals. It is possible, therefore, to obtain thermograms of the standard minerals for known weights as small as desired. The thermal characteristics of a given material may be most conveniently presented for quantitative analysis in the form of a curve of peak de-

CONCLUSIONS

flections of the thermogram versus weight of material for each of the characteristic reactions of the material. Standard thermograms should be obtained, therefore, for known weights throughout the range 0.1 gram to 0.3 gram of sample.

3. There is no basis for the assumption that the displaced base line is a horizontal line. Rather, it is concluded that in general the displaced base line is inclined to the zero millivolt line. Select thermograms of a given mineral may be used to locate those portions of the thermogram of that material which are tangent to the displaced base line. Thermograms of a mixture, may be analyzed by drawing the displaced base line tangent to those parts of the thermogram known to be inactive.

4. The inaccuracies which are inherent with the techniques of differential thermal analysis of materials as variable as are clays, are so great as to preclude the use of the method for quantitative analysis, unless a very large number of tests are run on different weights of each material, and the results of the tests on each weight averaged together. Not only

must a large number of tests be run, but the tests must be made with the same apparatus, preferably by the same individuals. This would prevent errors arising from slight differences in technique and procedure, and from differences in equipment arrangements and calibrations from entering into results.

5. The 1750 watt furnaces become so stabilized after a few runs that a reliable differential thermal curve is obtainable. This fact was well proven in the many repeat tests wherein any varying induced voltage in the thermocouple would have caused the thermogram to deviate from its straight line form. With care in setting the compensating rheostat, a uniform heating rate can be obtained with the 1750 furnaces.

APPENDIX I

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APPENDIX II

CALCULATION OF ERRORS

IN OBSERVATIONS OF PEAK POSITIONS OF F-12 ANALYSIS

See reference 7 for definitions and proofs of terms used.

Mean error in a single observation ≡ s.d. $= \frac{\Sigma v}{\sqrt{n(n-1)}}$

Mean error of the mean value of a series of values ≡ A.D.

$$A.D. = \frac{\Sigma v}{n\sqrt{(n-1)}}$$

$A.D. = \frac{s.d.}{\sqrt{n}}$ therefore $n = \left(\frac{s.d.}{A.D.}\right)^2$

where v ≡ Residual in a single reading (i.e. mean value of a series minus a single reading of the series)

n ≡ number of observations entering computation of mean value from which residuals are computed.

0.5 gram samples:

2'nd Endothermic Reaction

$$s.d. = \frac{0.54}{\sqrt{5\ (4)}} = \frac{0.54}{4.47} = 0.121$$

$$A.D. = \frac{0.54}{5\sqrt{4}} = 0.054$$

Exothermic Reaction

$$s.d. = \frac{0.52}{\sqrt{20}} = 0.1165$$

$$A.D. \quad \frac{0.52}{5\sqrt{4}} = 0.052$$

APPENDIX II

CALCULATIONS OF ERRORS

IN OBSERVATION OF PEAK REACTIONS OF B-12 ALLOY [illegible]

0.5 gram samples:

2'nd Endothermic Reaction

$$s.d. = \frac{1.99}{\sqrt{16(15)}} = \frac{1.99}{\sqrt{240}} = \frac{1.99}{15.5} = 0.128$$

$$S.D. = \frac{1.99}{16\sqrt{15}} = \frac{1.99}{62} = 0.032$$

Exothermic Reaction

$$s.d. = \frac{2.12}{\sqrt{240}} = \frac{2.12}{15.5} = 0.141$$

$$S.D. = \frac{2.12}{62} = 0.034$$

0.7 gram samples

2'nd Endothermic Reaction

$$s.d. = \frac{0.10}{\sqrt{3(2)}} = \frac{0.10}{2.45} = 0.04$$

$$S.D. = \frac{0.10}{3\sqrt{2}} = 0.0236$$

Exothermic Reaction

$$s.d. = \frac{0.44}{2.45} = 0.179$$

$$S.D. = \frac{0.44}{4.25} = 0.103$$

0.8 gram samples:

2'nd Endothermic Reaction

$$s.d. = \frac{0.22}{\sqrt{3(2)}} = \frac{0.22}{2.45} = 0.09$$

$$p.e. = \frac{0.22}{3\sqrt{2}} = 0.052$$

Exothermic Reaction

$$s.d. = \frac{0.56}{2.45} = 0.229$$

$$p.e. = \frac{0.56}{4.25} = 0.132$$

Calculation of number of tests required to give 2'nd endothermic reaction of 0.6 gram samples within 5% of true value.

$$0.6 \text{ gram} = \frac{0.6}{0.7} = 85.7\% \text{ of standard } 0.7 \text{ gram sample.}$$

80% of 0.7 gram = 0.56 gram

90% of 0.7 gram = 0.63 gram

From Figure 4

wt. clay mineral in sample	reaction in millivolts
.56	.495
.60	.510
.63	.521

p.e. must be $\eqsim (.52 - .51 = .01)$ to distinguish between sample weights of .60 + .63 grams.

Therefore number of tests required $= \left(\frac{.13}{.01}\right)^2 = 169$

APPENDIX IV

Calculation of Relative Thermal Capacities of Sample and Sample Holder.

Sample holder:

wt. = 203.0 grams.

mat'l = nickle

specific heat = 0.12 $\frac{\text{cal.}}{\text{gm.-}^\circ\text{C}}$ at 100 °C (reference Handbook of Chemistry and Physics, 27th Edition)

Sample:

wt. = 0.7 grams.

mat'l = clay mineral

specific heat = 0.22 $\frac{\text{cal.}}{\text{gm.-}^\circ\text{C}}$ at 100 °C

(ref. Handbook of Chemistry and Physics)

To raise temperature of sample 10 °C requires:

0.7 times 0.22 times 10 = 1.54 calories.

This quantity of heat would cool the sample holder

$$\frac{1.54}{203 \times .12} = .063 \text{ °C}$$

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